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Principal Investigator: El-Sayed, Mostafa A.
Award ID: 0240380
Organization: GA Tech Res Corp - GIT
Submitted By:

Title:
The Stability of Colloidal Metallic Nanoparticles in Reactive Chemical Environments

Project Participants

Senior Personnel

Name: El-Sayed, Mostafa
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Wang, Zhong
Worked for more than 160 Hours: No
Contribution to Project:
He is not involved actively in this research now, only on

Post-doc

Graduate Student

Undergraduate Student

Technician, Programmer

Other Participant

Research Experience for Undergraduates

Organizational Partners

Other Collaborators or Contacts

none

Activities and Findings

Research and Education Activities:
The research carried out involved the synthesis of platinum nanoparticles of different sizes and shapes and capped with PVP or other polymers such as polymethyl acrylates. TEM was used to determine the size and shape distributions and their changes during their catalytic activity in colloidal solutions.

Two reactions were studied. A gentle reaction involving electron transfer reaction at near room temperature between S2O3= and

Fe(CN)63-. The other is the Suzuki C-C coupling reaction between lodo benzene and phenol-boronic acid at 1000C.

Ms. Radha Narayanan has developed both the synthetic skills as well as the use of TEM and high resolution TEM techniques in this work. Furthermore, she was trained in writing and submitting papers by electronic paragon ACS technique.

Ms Radha Narayanan has secured an Academic job at the University of Rhode Island after two years of postdoctoral work.

Ms. Rachel Givens has continued her summer research and education working towards a graduate degree in our laboratory on nanocatalysis.

Findings:

FTIR spectroscopy has been used to study the binding geometry of polyacrylate capping material on cubic and tetrahedral platinum nanoparticles. It is proposed that the capping material forms an ester-like linkage to the Pt surface on the tetrahedral shapes through the hydroxyl oxygen atom of the carboxylic acid moiety of the polyacrylate (linear adsorption configuration). On the cubic particle, the adsorption occurs through both of the carboxylic oxygen atoms (bridge adsorption configuration). These shaped nanoparticles are synthesized by changing the starting ratio of the capping material to that of the Pt salt. The results are discussed in terms of the effect of changing the concentration of the polyacrylate capping material on the mode of bonding to the surface. This might be a factor in determining the final shape that is formed.

Nanocatalysis is a rapidly growing field that has undergone an explosive growth during the past decade. Nanoparticles have a large surface-to-volume ratio compared to other bulk catalytic materials, which make them attractive to use as catalysts. The surface atoms of nanoparticles are very active and this raises the possibility that the surface atoms could be so active that they could cause changes in the size and shape of the nanoparticles during the course of catalysis. In the bulk of the literature in the nanocatalysis field, there has not been an examination of what happens to the nanocatalysts during the course of its catalytic function. This kind of examination is necessary in order to truly examine the usefulness of nanoparticles as catalysts. In addition, these kinds of studies could also provide clues on how to design better catalysts.

Spherical, tetrahedral, and cubic shaped platinum nanoparticles in colloidal solution have been used to catalyze the electron transfer reaction between hexacyanoferrate and thiosulfate ions. The stability of the spherical PVP-Pt nanoparticles during the electron transfer reaction has been examined. The nanoparticles become slightly smaller after the first and second cycles of the reaction. In the presence of just the hexacyanoferrate (III) ions, it is observed that there is a large reduction in the size of the nanoparticles while in the presence of thiosulfate ions, the nanoparticles maintain their size. The hexacyanoferrate (III) ions could dissolve Pt atoms from the surface of the nanoparticles and form a complex via the cyanide group and this could explain the reduction in the nanoparticle

size. The thiosulfate binds to the nanoparticle surface via the sulfur group. Based on these observations, we propose that the mechanism of the reaction involves thiosulfate ions binding to the nanoparticle surface and reacting with hexacyanoferrate (III) ions in solution.

We have also conducted this reaction using tetrahedral PVP-Pt nanoparticles and cubic polyacrylate-Pt nanoparticles as catalysts. It is observed that dissolution of Pt atoms on the corners and edges occur after the first and second cycle of the reaction for both tetrahedral and cubic Pt nanoparticles. The dissolution of the corner and edge atoms is faster for the tetrahedral Pt nanoparticles than for the cubic Pt nanoparticles. Dissolution of atoms in the corners and edges of the tetrahedral and cubic nanoparticles also occur in the presence of hexacyanoferrate (III) ions and the nanoparticles maintain their shape in the presence of thiosulfate ions. This supports the mechanism we proposed for this reaction.

During the first forty minutes of the reaction, it is observed that there are no shape changes and as a result the shape dependence on the catalytic activity can be examined. The activation energy obtained using the spherical, tetrahedral, and cubic platinum nanoparticles are correlated with the fraction of surface atoms on the corners and edges of each type of particle. It is observed that the tetrahedral nanoparticles with the greatest fraction of atoms on their defective corners and edges are the most catalytically active while the cubic nanoparticles with the smallest fraction of atoms on the defective corners and edges are the least catalytically active. The spherical nanoparticles have a catalytic activity that is intermediate to that observed with the tetrahedral and cubic nanoparticles and have an intermediate fraction of atoms on the defective corners and edges. During the course of the entire reaction (2 days), it is observed that dissolution of atoms on the corners and edges of the tetrahedral and cubic nanoparticles result in distorted tetrahedral and distorted cubic nanoparticles. It is observed that with the distortion in the shape of the tetrahedral and cubic nanoparticles, there is a corresponding change in the activation energy of the reaction.

A detailed examination of the stability of spherical palladium nanoparticles in colloidal solution used to catalyze the Suzuki reaction has also been conducted. In the case of the Suzuki reaction with the spherical PVP-Pd nanoparticles as catalysts, it is observed that the Pd nanoparticles grow larger after the first cycle of the reaction due to Ostwald ripening processes. After the second cycle, the larger nanoparticles aggregate and precipitate out of solution leaving the smaller nanoparticles left in solution. In addition, studies in the presence of individual reactants have shown that the nanoparticles grow larger in the presence of iodobenzene and that the Ostwald ripening process is severely diminished in the presence of phenylboronic acid. These observations provide clues to the mechanism that the phenylboronic acid binds to the nanoparticle surface and reacts with iodobenzene via

collisional processes. A comparison between the use of PVP-Pd and dendrimer-Pd nanoparticles as catalysts was conducted in order to find out the effect of the stabilizer on the stability of the nanoparticles. It is observed that when PAMAM-OH Generation 4 dendrimer is used as the stabilizer for the Pd nanoparticles, the nanoparticles continue to grow during the second cycle of the Suzuki reaction. The higher the generation of the dendrimer, the better its capping action is. As a result, the strong capping action of the dendrimer results in the nanoparticles being more resistant to aggregation and precipitation. Studies in the presence of individual reactants support the proposed mechanism developed with the studies on the PVP-Pd nanoparticles.

In the literature, there have been recent studies that have shown that platinum complexes can catalyze the Suzuki reaction, but spherical platinum nanoparticles were found to not catalyze the Suzuki reaction. Since we have shown previously that the tetrahedral PVP-Pt nanoparticles can catalyze the electron transfer reaction, we decided to see if the colloidal tetrahedral Pt nanoparticles can catalyze the Suzuki reaction. It is observed that the tetrahedral Pt nanoparticles can catalyze the Suzuki reaction, but is not as catalytically active as the spherical palladium nanoparticles. In addition, it is observed that the tetrahedral platinum nanoparticles transform into the more stable spherical shape during the Suzuki reaction and in the presence of the all conditions except in the presence of phenylboronic acid. After the second cycle of the Suzuki reaction, it is observed that the transformed spherical nanoparticles become larger in size. In the presence of phenylboronic acid, the Pt nanoparticles maintain their tetrahedral shape and are similar in size to the tetrahedral Pt nanoparticles before any perturbations. As a result, these results also support the mechanism we have proposed for the Suzuki reaction.

FTIR has been used to investigate the mode of binding of phenylboronic acid to the palladium nanoparticle surface. It was determined that the phenylboronate anion binds to the palladium nanoparticle surface by the bridged mode of binding through the O- group. It was also determined that iodobenzene does not interact with the nanoparticle surface since there are no shifts in the characteristic infrared vibrational modes associated with iodobenzene. The FTIR studies confirm the mechanism of the Suzuki reaction we proposed previously and also provide information on the mode of binding of the phenylboronic acid to the nanoparticle surface.

We have a written an invited review article in the journal Chemical Reviews on the chemistry and properties of metal nanoparticles of different shapes. We have included a section on nanocatalysis in which we summarize our work on the use of different shaped platinum nanoparticles as catalysts for the electron transfer reaction and the Suzuki cross-coupling reaction. We also discuss the changes in the shape and size of the nanoparticles that occur during the course of these reactions. In addition, we are also in the process of writing an invited feature article in Journal of

Physical Chemistry B that focuses entirely on our nanocatalysis work that we have conducted up to this point.

Raman spectroscopy has been used to investigate the interaction of thiosulfate and hexacyanoferrate (III) ions on the platinum nanoparticle surface. It is observed that there is a mixture of binding that occurs in which the thiosulfate ions bind to the nanoparticle surface via the S- group and the O- group since both the Pt-S bond and the Pt-O bond is observed. It is also found that the hexacyanoferrate (III) ions also interact with the platinum nanoparticle surface and forms the Pt-CN complex. During the reaction, the concentration of the thiosulfate ions is 10 times greater than that of the hexacyanoferrate (III) ions. As a result, in the reaction conditions, the hexacyanoferrate (III) ions preferentially react with the adsorbed thiosulfate since there would be very few sites where it can interact with the platinum nanoparticles. As a result, the Raman study confirms the mechanism of the electron transfer reaction that we proposed previously and also provides the mode of binding of the thiosulfate ions onto the platinum nanoparticle surface.

Since these studies have shown that colloidal metal nanoparticles are unstable and undergo changes in their morphology (changes in the size and shape) during their catalytic function, there is a need to use alternative types of nanocatalysts. One possibility is to use supported metal nanoparticles as catalysts for a variety of reactions. Since carbon is a very common support material used for the preparation of supported nanoparticles, we have used this in our investigations. The use of carbon supported tetrahedral PVP-Pt nanoparticles as catalysts for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene has been compared to that of the colloidal tetrahedral PVP-Pt nanoparticles studied previously. It is determined that the carbon supported tetrahedral nanoparticles are more catalytically active than the colloidal tetrahedral Pt nanoparticles, but also have poor recycling potential like the colloidal platinum nanoparticles. In addition, it is determined that the carbon supported tetrahedral platinum nanoparticles transform into carbon supported spherical platinum nanoparticles more effectively than the colloidal platinum nanoparticles and this could be due to the low quantity of support that the nanoparticles are adsorbed onto. In addition, the Ostwald ripening process occurs at a faster rate in the case of the carbon supported platinum nanoparticles compared to the colloidal platinum nanoparticles. The more effective shape transformation process and the faster rate of nanoparticle growth could be due to the tetrahedral nanoparticles being adsorbed in close proximity to each other onto the carbon support.

The use of carbon supported spherical palladium nanoparticles as catalysts for the Suzuki reaction has also been compared to that of the colloidal spherical palladium nanoparticles studied previously. It is observed that the carbon supported spherical palladium nanoparticles are less catalytically active than the colloidal spherical palladium nanoparticles during the first cycle of the Suzuki reaction, but the supported palladium nanoparticles demonstrate almost double the recycling

potential than that observed with the colloidal spherical palladium nanoparticles. It is observed that the carbon supported spherical palladium nanoparticles continue to grow in size after the first and second cycle unlike the colloidal spherical palladium nanoparticles. The presence of the large amount of the carbon support could account for the continued growth of the nanoparticles that occur and also the preservation of the catalytic activity during the second cycle of the Suzuki reaction.

In addition, the effect of catalyzing a gas-phase reaction such as the propene hydrogenation reaction with carbon supported tetrahedral platinum nanoparticles has also been investigated. From GC-MS studies, it is determined that the carbon supported tetrahedral platinum nanoparticles do indeed catalyze the propene hydrogenation reaction and this is the first report of supported tetrahedral platinum nanoparticles catalyzing this gas-phase reaction. It is observed that during the propene hydrogenation reaction, there is a greater percentage of distorted carbon supported tetrahedral platinum nanoparticles compared to before the reaction. This suggests that the sharp corners and edges of the tetrahedral platinum nanoparticles are very reactive and results in the dissolution of the atoms on the corners and edges. This is similar results to those we observed previously with the colloidal tetrahedral platinum nanoparticles catalyzing the electron transfer reaction in solution.

We identified a Prussian blue analogue that forms in solution when platinum nanoparticles are used to catalyze the electron transfer reaction between ferricyanide and thiosulfate. We found strong evidence that the Prussian blue analogue, which is composed of several different species of Pt-Fe complexes, is formed prior to the oxidation of thiosulfate. This result signifies that the platinum particle is not fully stable in solution, and serves not as a catalyst but as a reactant that complexes with the ferricyanide and then undergoes reduction by thiosulfate. This result agrees with an earlier paper published in the previous support period that identifies a surface complex via Raman spectroscopy that forms in solution during the electron transfer reaction between thiosulfate and ferricyanide catalyzed by platinum nanoparticles.

We have discovered a new nanocatalyst shape that has superior catalytic activation energy for the electron-transfer reaction between thiosulfate and ferricyanide, namely the platinum nanostar. The nanostar was imaged using high resolution TEM and found to be single crystalline with many 'arms' protruding off of a central seed particle used in the synthesis process. We found that the single crystalline property of the nanoparticle provided several high index facets to the reactants in solution that resulted in higher catalytic activities.

Training and Development:

It is obvious that Ms. Radha Narayanan has developed her research skills. She now comes with proposal for new experiments to do. She has given talks and posters at several ACS national, regional, and local meetings such as SERMACS, ACS National Meetings, Colloids and Surface Science Symposium, MRS National Meeting, etc.

Last two summers, Ms Rachel Given was partially supported by this grant. She is one of our best undergraduate students. She has a double major in Chemistry and Physics. She won a good
number of Prizes here at Tech. She is going to be a stellar chemist in the future. She has been accepted by Berkeley, Stanford and Georgia Tech graduate schools. She has chosen to attend Georgia Tech for graduate studies in Chemistry and continues to work on surface supported catalytic reactions in solution.

Outreach Activities:

We worked with a high school student (Mr. Matlock Rodgers) who

entered in a science fair competition in his school, in his county
and the State of Georgia and ranked No. 1 in all three.

Attracting Ms Rachel Givens to chemical research and to nanocatalysis is the best outreach we can accomplish. She worked with us for two sequential summers and now is continuing her studies in the graduate school at Georgia Tech.

Journal Publications

Radha Narayanan, Mostafa A. El-Sayed, "Effect of Catalysis on the Stability of Metallic Nanoparticles:
Suzuki Reaction Catalyzed by PVP-Palladium Nanoparticles?", Journal of the American Chemical Society, p. 8340, vol. 125, (2003). Published,

Radha Narayanan, Mostafa A. El-Sayed, "?Effect of Catalytic Activity on the Metallic Nanoparticle Size
Distribution: Electron-Transfer Reaction between Fe(CN)6 and
Thiosulfate Ions Catalyzed by PVP-Platinum Nanoparticles?", Journal of Physical Chemistry B, p. 12416, vol. Vol 107, (2003). Published,

Janet Petroski and Mostafa A. El-Sayed, ""FTIR Study of the Adsorption of the Capping Material to Different
Platinum Nanoparticle Shapes"", Journal of Physical Chemistry A, p. 8371, vol. Vol 107, (2003). Published,

Radha Narayanan and Mostafa A. El-Sayed, "Effect of Catalysis in Colloidal Solution on the Tetrahedral and Cubic Nanoparticle SHAPE: Electron Transfer Reaction Catalyzed by Platinum Nanoparticles", Journal of Physical Chemistry B, p. 5726, vol. 108, (2004). Published,

Radha Narayanan and Mostafa A. El-Sayed, "Changing Catalytic Activity During Colloidal Platinum Nanocatalysis Due to Shape Changes: Electron Transfer Reaction", Journal of the American Chemical Society, p. 7194, vol. 126, (2004). Published,

Radha Narayanan and Mostafa A. El-Sayed, "Effect of Colloidal Catalysis on the Nanoparticle Size Distribution: Dendrimer-Pd vs. PVP-Pd Nanoparticles Catalyzing the Suzuki Coupling Reaction", Journal of Physical Chemistry B, p. 8572, vol. 108, (2004). Published,

Radha Narayanan and Mostafa A. El-Sayed, "Shape-Dependent Catalytic Activity of Platinum Nanoparticles in Colloidal Solution", Nano Letters, p. 1343, vol. 4, (2004). Published,

Radha Narayanan and Mostafa A. El-Sayed, "Effect of Colloidal Nanocatalysis on the Metallic Nanoparticle Shape: The Suzuki Reaction", Langmuir, p. 2027, vol. 21, (2005). Published,

Radha Narayanan and Mostafa A. El-Sayed, "FTIR Study of the Mode of Binding of the Reactants on the Pd Nanoparticle Surface during the Catalysis of the Suzuki Reaction", Journal of Physical Chemistry B, p. , vol. 109, (2005). Published,

Burda, C.; Chen, X.; Narayanan, R.; and El-Sayed, M. A., "The Chemistry and Properties of Nanocrystals of Different Shapes", Chemical Reviews, p. , vol. 105, (2005). Published,

Narayanan, R.; and El-Sayed, M. A., "Colloidal Catalysis with Transition Metal Nanoparticles: Effect of Nanoparticle Shape on Catalysis and the Effect of Catalysis on the Nanoparticle Shape and Size", Journal of Physical Chemistry B, p. , vol. , ( ). Invited Feature Article in Preparation,

Narayanan, R.; and El-Sayed, M. A., "Raman Studies on the Interactions of the Reactants on the Platinum Nanoparticle Surface During the Electron Transfer Reaction", J. Phys. Chem. B,, p. , vol. 109(39), (2005). In preparation for submission,

Narayanan, R.; and El-Sayed, M. A., "Carbon Supported Spherical Palladium Nanoparticles as Potential Recyclable Catalysts for the Suzuki Reaction and the Effect of Catalysis on the Nanoparticle Size", J. Catal.,, p. 348, vol. 234(2),, (2005). Published,

Narayanan, R.; El-Sayed, M. A., "Catalysis with Metallic Nanoparticles: The Good and the Bad", Chimica Oggi/Chem. Today-Int. J. Chem. Biotech., p. 84, vol. 25, (2007). Published,

Narayanan, R.; El-Sayed, M. A, "Catalysis with Transition Metal Nanoparticles in Colloidal Solution: Nanoparticle Shape Dependence and Stability", J. Phys. Chem. B, p. 12663, vol. 109(26, (2005). Published,

Burda, C.; Chen, X.; Narayanan, R.; El-Sayed, M. A., "The Chemistry and Properties of Nanocrystals of Different Shapes",., ?,),-1102", Chem. Rev, p. 1025, vol. 105(4, (2005). Published,

Mahmoud, MA; Ei-Sayed, MA, "Reaction of platinum nanocatalyst with the ferricyanide reactant to produce Prussian blue analogue complexes", JOURNAL OF PHYSICAL CHEMISTRY C, p. 17180, vol. 111, (2007). Published, 10.1021/jp709735

Narayanan, R; Tabor, C; El-Sayed, MA, "Can the observed changes in the size or shape of a colloidal nanocatalyst reveal the nanocatalysis mechanism type: Homogeneous or heterogeneous?", TOPICS IN CATALYSIS, p. 60, vol. 48, (2008). Published, 10.1007/s11244-008-9057-

Narayanan, R; El-Sayed, MA, "Some aspects of colloidal nanoparticle stability, catalytic activity, and recycling potential", TOPICS IN CATALYSIS, p. 15, vol. 47, (2008). Published, 10.1007/s11244-007-9029-

Mahmoud, MA; El-Sayed, MA, "Comparative study of the assemblies and the resulting plasmon fields of Langmuir-Blodgett assembled monolayers of silver nanocubes and gold nanocages", JOURNAL OF PHYSICAL CHEMISTRY C, p. 14618, vol. 112, (2008). Published, 10.1021/jp804049

Mahmoud, MA; Tabor, CE; El-Sayed, MA; Ding, Y; Wang, ZL, "A new catalytically active colloidal platinum nanocatalyst: The multiarmed nanostar single crystal", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, p. 4590, vol. 130, (2008). Published, 10.1021/ja710646

Neretina, S; Qian, W; Dreaden, E; Ei-Sayed, MA; Hughes, RA; Preston, JS; Mascher, P, "Plasmon field effects on the nonradiative relaxation of hot electrons in an electronically quantized system: CdTe-Au core-shell nanowires", NANO LETTERS, p. 2410, vol. 8, (2008). Published, 10.1021/nl801303

Books or Other One-time Publications

Christopher Tabor, Radha Narayanan, Mostafa A. El-Sayed, "Catalysis with Transition Metal Nanoparticles in Colloidal Solution: Heterogeneous or Homogeneous", (2008). Book, Accepted
Editor(s): Dr. Robert Rioux
Collection: Model Systems in Catalysis: From Single Crystals and Size-Selected Clusters to Supported Enzyme Mimics
Bibliography: Tabor, C; Narayanan, R; El-Sayed, M.A.; "Catalysis with Transition Metal Nanoparticles in Colloidal Solution: Heterogeneous or Homogeneous?" 2008. In Press

Web/Internet Site

Other Specific Products

Contributions

Contributions within Discipline:

The contribution of our work impacts two discipline, nanoscience and catalysis. The following are our contributions to these fields:

FTIR spectroscopy has been used to study the binding geometry of polyacrylate capping material on cubic and tetrahedral platinum nanoparticles. It is proposed that the capping material forms an ester-like linkage to the Pt surface

on the tetrahedral shapes through the hydroxyl oxygen atom of the carboxylic acid moiety of the polyacrylate (linear adsorption configuration). On the cubic particle, the adsorption occurs through both of the carboxylic oxygen atoms (bridge adsorption configuration). These shaped nanoparticles are synthesized by changing the starting ratio of the capping material to that of the Pt salt. The results are discussed in terms of the effect of changing the concentration of the polyacrylate capping material on the mode of bonding to the surface. This might be a factor in determining the final shape that is formed.

Nanocatalysis is a rapidly growing field that has undergone an explosive growth during the past decade. Nanoparticles have a large surface-to-volume ratio compared to other bulk catalytic materials, which make them attractive to use as catalysts. The surface atoms of nanoparticles are very active and this raises the possibility that the surface atoms could be so active that they could cause changes in the size and shape of the nanoparticles during the course of catalysis. In the bulk of the literature in the nanocatalysis field, there has not been an examination of what happens to the nanocatalysts during the course of its catalytic function. This kind of examination is necessary in order to truly examine the usefulness of nanoparticles as catalysts. In addition, these kinds of studies could also provide clues on how to design better catalysts.

Spherical, tetrahedral, and cubic shaped platinum nanoparticles in colloidal solution have been used to catalyze the electron transfer reaction between hexacyanoferrate and thiosulfate ions. The stability of the spherical PVP-Pt nanoparticles during the electron transfer reaction has been examined. The nanoparticles become slightly smaller after the first and second cycles of the reaction. In the presence of just the hexacyanoferrate (III) ions, it is observed that there is a large reduction in the size of the nanoparticles while in the presence of thiosulfate ions, the nanoparticles maintain their size. The hexacyanoferrate (III) ions could dissolve Pt atoms from the surface of the nanoparticles and form a complex via the cyanide group and this could explain the reduction in the nanoparticle size. The thiosulfate binds to the nanoparticle surface via the sulfur group. Based on these observations, we propose that the mechanism of the reaction involves thiosulfate ions binding to the nanoparticle surface and reacting with hexacyanoferrate (III) ions in solution.

We have also conducted this reaction using tetrahedral PVP-Pt nanoparticles and cubic polyacrylate-Pt nanoparticles as catalysts. It is observed that dissolution of Pt atoms on the corners and edges occur after the first and second cycle of the reaction for both tetrahedral and cubic Pt nanoparticles. The dissolution of the corner and edge atoms is faster for the tetrahedral Pt nanoparticles than for the cubic Pt nanoparticles. Dissolution of atoms in the corners and edges of the tetrahedral and cubic nanoparticles also occur in the presence of hexacyanoferrate (III) ions and the nanoparticles maintain their shape in the presence of thiosulfate ions. This supports the mechanism we proposed for this reaction.

During the first forty minutes of the reaction, it is observed that there are no shape changes and as a result the shape dependence on the catalytic activity can be examined. The activation energy obtained using the spherical, tetrahedral, and cubic platinum nanoparticles are correlated with the fraction of surface atoms on the corners and edges of each type of particle. It is observed that the tetrahedral nanoparticles with the greatest fraction of atoms on their defective corners and edges are the most catalytically active while the cubic nanoparticles with the smallest fraction of atoms on the defective corners and edges are the least catalytically active. The spherical nanoparticles have a catalytic activity that is intermediate to that observed with the tetrahedral and cubic nanoparticles and have an intermediate fraction of atoms on the defective corners and edges. During the course of the entire reaction (2 days), it is observed that dissolution of atoms on the corners and edges of the tetrahedral and cubic nanoparticles result in distorted tetrahedral and distorted cubic nanoparticles. It is observed that with the distortion in the shape of the tetrahedral and cubic nanoparticles, there is a corresponding change in the activation energy of the reaction.

A detailed examination of the stability of spherical palladium nanoparticles in colloidal solution used to catalyze the Suzuki reaction has also been conducted. In the case of the Suzuki reaction with the spherical PVP-Pd nanoparticles as catalysts, it is observed that the Pd nanoparticles grow larger after the first cycle of the reaction due to Ostwald ripening processes. After the second cycle, the larger nanoparticles aggregate and precipitate out of solution leaving the smaller nanoparticles left in solution. In addition, studies in the presence of individual reactants have shown that the nanoparticles grow larger in the presence of iodobenzene and that the Ostwald ripening process is severely diminished in the presence of phenylboronic acid. These observations provide clues to the mechanism that the phenylboronic acid binds to the nanoparticle surface and reacts with iodobenzene via collisional processes. A comparison between the use of PVP-Pd and dendrimer-Pd nanoparticles as catalysts was conducted in order to find out the effect of the stabilizer on the stability of the nanoparticles. It is observed that when PAMAM-OH Generation 4 dendrimer is used as the stabilizer for the Pd nanoparticles, the nanoparticles continue to grow during the second cycle of the Suzuki reaction. The higher the generation of the dendrimer, the better its capping action is. As a result, the strong capping action of the dendrimer results in the nanoparticles being more resistant to aggregation and precipitation. Studies in the presence of individual reactants support the proposed mechanism developed with the studies on the PVP-Pd nanoparticles.

In the literature, there have been recent studies that have shown that platinum complexes can catalyze the Suzuki reaction, but spherical platinum nanoparticles were found to not catalyze the Suzuki reaction. Since we have shown previously that the

tetrahedral PVP-Pt nanoparticles can catalyze the electron transfer reaction, we decided to see if the colloidal tetrahedral Pt nanoparticles can catalyze the Suzuki reaction. It is observed that the tetrahedral Pt nanoparticles can catalyze the Suzuki reaction, but is not as catalytically active as the spherical palladium nanoparticles. In addition, it is observed that the tetrahedral platinum nanoparticles transform into the more stable spherical shape during the Suzuki reaction and in the presence of the all conditions except in the presence of phenylboronic acid. After the second cycle of the Suzuki reaction, it is observed that the transformed spherical nanoparticles become larger in size. In the presence of phenylboronic acid, the Pt nanoparticles maintain their tetrahedral shape and are similar in size to the tetrahedral Pt nanoparticles before any perturbations. As a result, these results also support the mechanism we have proposed for the Suzuki reaction.

FTIR has been used to investigate the mode of binding of phenylboronic acid to the palladium nanoparticle surface. It was determined that the phenylboronate anion binds to the palladium nanoparticle surface by the bridged mode of binding through the O- group. It was also determined that iodobenzene does not interact with the nanoparticle surface since there are no shifts in the characteristic infrared vibrational modes associated with iodobenzene. The FTIR studies confirm the mechanism of the Suzuki reaction we proposed previously and also provide information on the mode of binding of the phenylboronic acid to the nanoparticle surface.

We have a written an invited review article in the journal Chemical Reviews on the chemistry and properties of metal nanoparticles of different shapes. We have included a section on nanocatalysis in which we summarize our work on the use of different shaped platinum nanoparticles as catalysts for the electron transfer reaction and the Suzuki cross-coupling reaction. We also discuss the changes in the shape and size of the nanoparticles that occur during the course of these reactions. In addition, we are also in the process of writing an invited feature article in Journal of Physical Chemistry B that focuses entirely on our nanocatalysis work that we have conducted up to this point.

Raman spectroscopy has been used to investigate the interaction of thiosulfate and hexacyanoferrate (III) ions on the platinum nanoparticle surface. It is observed that there is a mixture of binding that occurs in which the thiosulfate ions bind to the nanoparticle surface via the S- group and the O- group since both the Pt-S bond and the Pt-O bond is observed. It is also found that the hexacyanoferrate (III) ions also interact with the platinum nanoparticle surface and forms the Pt-CN complex. During the reaction, the concentration of the thiosulfate ions is 10 times greater than that of the hexacyanoferrate (III) ions. As a result, in the reaction conditions, the hexacyanoferrate (III) ions preferentially react with the adsorbed thiosulfate since there would be very few sites where it can interact with the platinum nanoparticles. As a result, the Raman study confirms the mechanism of the electron transfer reaction that we proposed

previously and also provides the mode of binding of the thiosulfate ions onto the platinum nanoparticle surface.

Since these studies have shown that colloidal metal nanoparticles are unstable and undergo changes in their morphology (changes in the size and shape) during their catalytic function, there is a need to use alternative types of nanocatalysts. One possibility is to use supported metal nanoparticles as catalysts for a variety of reactions. Since carbon is a very common support material used for the preparation of supported nanoparticles, we have used this in our investigations. The use of carbon supported tetrahedral PVP-Pt nanoparticles as catalysts for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene has been compared to that of the colloidal tetrahedral PVP-Pt nanoparticles studied previously. It is determined that the carbon supported tetrahedral nanoparticles are more catalytically active than the colloidal tetrahedral Pt nanoparticles, but also have poor recycling potential like the colloidal platinum nanoparticles. In addition, it is determined that the carbon supported tetrahedral platinum nanoparticles transform into carbon supported spherical platinum nanoparticles more effectively than the colloidal platinum nanoparticles and this could be due to the low quantity of support that the nanoparticles are adsorbed onto. In addition, the Ostwald ripening process occurs at a faster rate in the case of the carbon supported platinum nanoparticles compared to the colloidal platinum nanoparticles. The more effective shape transformation process and the faster rate of nanoparticle growth could be due to the tetrahedral nanoparticles being adsorbed in close proximity to each other onto the carbon support.

The use of carbon supported spherical palladium nanoparticles as catalysts for the Suzuki reaction has also been compared to that of the colloidal spherical palladium nanoparticles studied previously. It is observed that the carbon supported spherical palladium nanoparticles are less catalytically active than the colloidal spherical palladium nanoparticles during the first cycle of the Suzuki reaction, but the supported palladium nanoparticles demonstrate almost double the recycling potential than that observed with the colloidal spherical palladium nanoparticles. It is observed that the carbon supported spherical palladium nanoparticles continue to grow in size after the first and second cycle unlike the colloidal spherical palladium nanoparticles. The presence of the large amount of the carbon support could account for the continued growth of the nanoparticles that occur and also the preservation of the catalytic activity during the second cycle of the Suzuki reaction.

In addition, the effect of catalyzing a gas-phase reaction such as the propene hydrogenation reaction with carbon supported tetrahedral platinum nanoparticles has also been investigated. From GC-MS studies, it is determined that the carbon supported tetrahedral platinum nanoparticles do indeed catalyze the propene hydrogenation reaction and this is the first report of supported tetrahedral platinum nanoparticles catalyzing this gas-phase reaction. It is observed that during the propene

hydrogenation reaction, there is a greater percentage of distorted carbon supported tetrahedral platinum nanoparticles compared to before the reaction. This suggests that the sharp corners and edges of the tetrahedral platinum nanoparticles are very reactive and results in the dissolution of the atoms on the corners and edges. This is similar results to those we observed previously with the colloidal tetrahedral platinum nanoparticles catalyzing the electron transfer reaction in solution.

We identified a Prussian blue analogue that forms in solution when platinum nanoparticles are used to catalyze the electron transfer reaction between ferricyanide and thiosulfate. We found strong evidence that the Prussian blue analogue, which is composed of several different species of Pt-Fe complexes, is formed prior to the oxidation of thiosulfate. This result signifies that the platinum particle is not fully stable in solution, and serves not as a catalyst but as a reactant that complexes with the ferricyanide and then undergoes reduction by thiosulfate. This result agrees with an earlier paper published in the previous support period that identifies a surface complex via Raman spectroscopy that forms in solution during the electron transfer reaction between thiosulfate and ferricyanide catalyzed by platinum nanoparticles.

We have discovered a new nanocatalyst shape that has superior catalytic activation energy for the electron-transfer reaction between thiosulfate and ferricyanide, namely the platinum nanostar. The nanostar was imaged using high resolution TEM and found to be single crystalline with many 'arms' protruding off of a central seed particle used in the synthesis process. We found that the single crystalline property of the nanoparticle provided several high index facets to the reactants in solution that resulted in higher catalytic activities.

Our past contributions has impacted (if not started) the field of Nanocatalysis. Our 1996 Science report was the begining of shape dependent nancatalysis (it is the second most cited paper in the field, the first being a review article).

Contributions to Other Disciplines:

The field of catalysis makes the largest contribution to our industrial output. Nanoparticles are predicted to have one of its important impacts on the field of catalysis, due to their large surface to volume ratio. In order to realize their impact, the important properties of the nanoparticles as they pertain to their catalytic function needs to be carefully examined. The results of our studies impacts directly the field of catalysis with nanoparticles. Nanoparticles are new types of catalysts. However, to use them, we need to understand their stability and the effect of catalysis on them.

Contributions to Human Resource Development:

We educate students in the fields of nanoscience as well as in the field of surface catalysis. These are two fields of the utmost importance to the future economic developments of our country.

My graduate student, Ms. Radha Narayanan, who has worked extensively in this project, is interested in pursuing an academic career after her Ph.D. studies. I have been involved in extensive mentoring to help her prepare for a future academic career.

She has accepted an Academic position at the University of Rhode Island.

Oue Bright undergraduate researcher, Ms Rachel Givens received some of our department's awards and was accepted by Berkely and Stanford chemistry graduate schools, but has chosen to attend Georgia Tech and pursue her Ph.D. in our group studying nanocatalysis.

Contributions to Resources for Research and Education:

In my group meetings, my students and I give several talks on the field of surface science and catalysis. I also gave a few lectures in our departmental course in nanoscience. I gave numerous seminars in many Universities around the country

on this topic. In addition, Ms. Radha Narayanan, my x- graduate student, has also given several talks on her work in this project at many local, regional, and national meetings.

Contributions Beyond Science and Engineering:

Hopefully, it will increase our catalytic power thus reducing the cost and increasing the benefits to the chemical, environmental and oil industries. It could also provide new directions toward the design of better catalysts in many industries, specially those in energy and environment.

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